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13. ABSTRACT (Maximum 200 words)

The difficulties in conventional density functional theory (DFT) are discussed. An alternative exact procedure, the Optimized Effective Potential (OEP) method, is discussed and its analytic properties that are significant in DFT are presented. The difficulties in solving the integral equation for the OEP are eliminated by the introduction of the Krieger-Li-Iafrate (KLI) approximation which leads to important analytic properties that are identical to those of the OEP. Detailed self-consistent calculations on atoms and negative ions demonstrate that the KLI yields results that are nearly identical to those of the OEP and are a significant improvement over those given by the local spin density approximation and its gradient corrected versions. Calculations have been extended to molecules in the exchange-only approximation and are close to Hartree-Fock results.

An accurate self-interaction-free correlation energy functional has been constructed from considerations of a homogeneous electron gas with an energy gap. Calculations on atoms, molecules and surfaces demonstrate that this functional is at least as accurate as any alternative generalized gradient approximation. The incorporation of contributions from low lying virtual states is being studied.

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Final Report on Application of the Optimized Effective Potential Method to Quantum Chemistry

Foreword

The development of density functional theory (DFT) beginning with the seminal work of Hohenberg and Kohn^{(1)(HK)} and Kohn and Sham^{(2)(KS)} in the mid 1960's has revolutionized the development of accurate quantum mechanical calculations of the ground state properties of atoms, molecules and solids. HK were able to show that for a given ground state density there exists a corresponding unique external potential (up to a trivial additive constant). Thus the many body wave-function of any quantum mechanical system can be considered to be a functional of the ground state density. Consequently, in addition to the expectation value of the external potential, all the other elements entering into a calculation of the ground state energy i.e. the kinetic energy and the expectation value of the electron-electron interaction, are also functionals of the ground state density, although the functional form of these latter two functionals are not given by the HK theorem. Furthermore, HK showed that when the ground state energy of the system was written in terms of these functionals, then the true energy of the system could be obtained by minimizing the energy functional with respect to the density, thus generalizing the variational theorem to DFT.

This theorem has been employed by KS who developed a computationally efficient means of performing ground state calculations by considering a corresponding system of non-interacting electrons with the same density moving in the same external potential as in the interacting system. They found that the exact ground state energy of the interacting system could then be written as the sum of the kinetic energy of the non-interacting system plus the average external potential, the Hartree energy and a non-classical term referred to as the exchange-correlation energy $E_{xc}[n]$, which is in general an unknown universal functional of the density n . They were able to show that the single particle Schrödinger equations satisfied by the orbitals in the non-interacting gas satisfy Hartree-like equations with the Hartree potential

corrected by an additional term, the so-called exchange-correlation potential, $V_{xc}[n]$, which is the functional derivative of the E_{xc} with respect to n just as the Hartree potential is the functional derivative of the Hartree energy with respect to n . The KS theory has been extended to the more accurate spin density functional theory by von Barth and Hedin⁽³⁾ for spin-polarized system in which the exchange-correlation energy functional is considered to be a functional of the separate spin densities and there are two exchange-correlation potentials, $V_{xc\sigma}$, corresponding to electrons with spin σ up or down.

Although the exact form of $V_{xc\sigma}[n_{\uparrow}, n_{\downarrow}]$ is not known in general, it is characterized by certain essential properties:

- 1) In the slowly varying density limit the exchange-only potential, $V_{x\sigma}$ should approach 2/3 of the Slater exchange potential⁽²⁾.
- 2) $V_{xc\sigma}(\mathbf{r})$ should be self-interaction-free⁽⁴⁾ so that if a system contains only one electron the $V_{xc\sigma}(\mathbf{r})$ exactly cancels the self-Hartree potential independent of the form of the external potential.
- 3) For systems containing a finite number of particles, $V_{xc\sigma} \rightarrow -1/r$ as $r \rightarrow \infty$ ⁽⁵⁾.
- 4) The energy eigenvalue, ϵ_m , of the highest occupied molecular orbital (HOMO) should equal the negative of the removal energy including all relaxation effects⁽⁶⁾.
- 5) $V_{xc\sigma}$ should exhibit an integer discontinuity, i.e. when the number of electrons in a system having discrete energy spectrum with filled subshells changes from N to $N + \delta$ (with δ being a positive infinitesimal) the $V_{xc\sigma}^{N + \delta}(\mathbf{r})$ will shift from $V_{xc\sigma}^N$ by a constant for finite r ^(7,8).

The local spin density (LSD) approximation^(2,3) plus gradient corrections, which is the approximation for E_{xc} and $V_{xc\sigma}$ nearly universally employed in DFT calculations, satisfies

property(1), but fails to satisfy the other properties. The fact that property (2) is not satisfied leads to a significant overestimate of the correlation energy⁽⁴⁾. The fact that property (3) is not satisfied results in inaccurate description of the potential in which the valence electrons move, leading to moderate discrepancies in the valence electron distribution as well as significant errors in ϵ_m . Thus property (4) is generally poorly satisfied with ϵ_m being $\approx 40\%$ too small in magnitude compared to the ionization energies of atoms. In addition, there are no stable negative ions predicted in disagreement with reality. Finally, the failure to satisfy property (5) leads to significant errors in the calculation of energy band gaps in semiconductors and insulators^(7,8) as well as violations of the principle of integer preference⁽⁹⁾, which requires that when molecules dissociate there is an integer number of electrons localized around each atom. However, the likelihood of ever finding a $V_{xc\sigma}([n_\sigma], r)$ that respects the principle of integer preference has been considered doubtful⁽¹⁰⁾. Moreover, no finite expansion in higher order derivatives of the spin density can account for the discontinuity in $V_{xc\sigma}$.⁽¹¹⁾

These facts require a reconsideration of density functional theory in order that these problems be addressed. Thus, as the first generation of DFT, the HK method, employing a Thomas-Fermi approximation for the kinetic energy functional gave way to the more accurate second generation KS method, which treated the kinetic energy exactly, a third generation DFT must employ expressions for E_{xc} which are explicit functionals of the occupied single particle orbitals $\phi_{i\sigma}$. Since the $\phi_{i\sigma}$ are functionals of the spin densities, such $E_{xc}[\{\phi_{i\sigma}\}]$ are implicit functionals of the n_σ but carry a great deal more information about the system. Thus, for example, the exact exchange energy functional is the orbital-dependent expression given in the Hartree-Fock (HF) approximation. However, unlike the HF method, in which the single particle orbitals satisfy Schrödinger-like equations with non-local exchange potentials which are different for each orbital, the Kohn-Sham method continues to treat all electrons with a given spin projection as moving in a single, local, multiplicative potential, thus enabling the application of this method to much larger systems than can be treated by the HF method. Moreover, the KS theory allows for the direct inclusion of correlation effects through the incorporation of a correlation energy functional into E_{xc} whereas the HF method can only include such effects through a complicated and slowly convergent perturbation theory calculation. Such a method also permits the use of simpler energy functionals with important self-interaction-corrections

(SIC) which are orbital dependent contributions as provided for example by Perdew and Zunger.⁽⁴⁾

The difficulty in employing orbital dependent exchange-correlation functionals arises from the fact that the corresponding exchange-correlation functionals, $V_{xc\sigma}$, cannot simply be obtained from $E_{xc}[\{\phi_{i\sigma}\}]$ because⁽¹²⁾ $\frac{\delta \phi_{i\sigma}}{\delta n_{\sigma}} \neq \left(\frac{\delta n_{\sigma}}{\delta \phi_{i\sigma}} \right)^{-1}$. Instead, a complicated integral equation must be solved anew for the optimized effective potential (OEP) $V_{xc\sigma}$, for each system. This was the situation when we began our investigations into the Application of the Optimized Effective Potential Method to Quantum Chemistry.

I. The Optimized Effective Potential (OEP) Method

In order to carefully investigate the application of the OEP method to quantum chemistry we have extended the derivation of the equation for the OEP, V_{xc}° , to the case of fractional occupancy⁽¹³⁾ for the exact exchange-only case and subsequently generalized this result to the general case of an arbitrary $E_{xc}[\{\phi_{i\sigma}\}]$.⁽¹⁴⁾ The need for such an investigation has already been discussed in the Foreword. In the following we shall summarize the most important results of our investigations as requested in the instructions for preparation of the final report and in each case provide the appropriate reference in which the details may be found.

We have carefully investigated the analytic properties of the exact $V_{xc\sigma}^\circ$ that follows from the integral equation and have shown⁽¹⁴⁾ that for arbitrary $E_{xc}[\{\phi_{i\sigma}\}]$

$$\bar{V}_{xc\sigma m}^\circ = \bar{v}_{m\sigma}^\circ \quad (1)$$

where the bar indicates the average value over the $\phi_{m\sigma}^\circ$ state. Here $m\sigma$ represents the highest (fractionally) occupied state of spin projection σ and $v_{m\sigma}$ corresponds to the single particle exchange-correlation potential that would enter into the equation $\delta E / \delta \phi_{m\sigma}^* = 0$ subject to $\phi_{m\sigma}$ being normalized to unity in a multi-potential theory.

From eq. (1) it immediately follows⁽¹⁴⁾ that

$$\epsilon_{m\sigma}^\circ = \bar{\epsilon}_{m\sigma}^{\circ MP} \quad (2)$$

Where $\epsilon_{m\sigma}^\circ$ is the OEP energy eigenvalue for the highest occupied state and $\bar{\epsilon}_{m\sigma}^{\circ MP}$ is the corresponding expectation value with respect to $\phi_{m\sigma}^\circ$ of the single particle hamiltonian for the $m\sigma$ state in a multi-potential theory. Equation (2), which is now generally referred to as the HOMO condition for the OEP, is very useful for checking the self-consistency of any "exact"

solution of the OEP integral equation. It was first derived for the exchange-only case by the P.I. and collaborators⁽¹⁵⁾ and immediately applied to test the accuracy of then recently reported exchange-only OEP results.⁽¹⁶⁾

More significantly, it follows from eq. (1) that in the exchange-only case in the slowly varying density limit, $V_{x\sigma} \rightarrow \frac{2}{3} V_{x\sigma}^s$ where $V_{x\sigma}^s$ is the Slater potential.⁽¹⁷⁾ Thus, without making any density functional approximation for E_x , it is possible to derive this fundamental result directly from the OEP integral equation.^(13, 14) Moreover, it also follows from eq (1) and the condition that $V_{x\sigma} \rightarrow 0$ as $r \rightarrow \infty$ that if $E_{x\sigma}$ includes the self-interaction terms that cancel the self-Hartree terms, terms^(13, 14) $V_{x\sigma} \rightarrow -1/r$ as $r \rightarrow \infty$. In addition, we have shown first in the exchange-only case⁽¹³⁾ and subsequently for a more general $E_{xc}[\{\phi_{i\sigma}\}]$ that $V_{x\sigma}^o$ has a discontinuity when a new spin sub-shell begins to be filled.⁽¹⁴⁾ Thus, the exact solution of the OEP integral equation would exhibit many of the important properties missing from the LSD approximations as well as those employing gradient corrections.

Furthermore, we have shown that Janak's theorem⁽¹⁸⁾ is satisfied for any $E_{xc}[\{\phi_{i\sigma}\}]$, but only for the highest partially occupied state of spin projection σ i.e.

$$\frac{dE^o}{df_{m\sigma}} = \epsilon_{m\sigma}^o(f_{m\sigma}) \quad (3)$$

where $f_{m\sigma}$ is the fractional occupancy of the $m\sigma$ state.⁽¹⁴⁾ In addition, we have proved⁽¹⁴⁾ that the electron spin densities and $\epsilon_{m\sigma}$ obtained by employing the OEP method differ by $O(\delta^2)$ from that given by the corresponding multi-potential theory where δ is a measure of the difference between the OEP and multi-potential wavefunctions. Thus, in the special case of exchange-only calculations, the OEP and Hartree-Fock densities are the same to $O(\delta^2)$ which should result in nearly identical values of all single particle expectation values. Moreover, in the exchange-only case we have shown^(13,14) that the OEP method satisfies Koopmans' theorem⁽²⁰⁾ for the highest occupied state i.e.

$$E^\circ(N) - E_u^\circ(N-1) = \epsilon_{m\sigma}^\circ \quad (4)$$

where the subscript u denotes the unrelaxed state i.e. the energy evaluated with the same orbitals with the $m\sigma$ orbital missing. It then follows from eqs. (2) and (4) that the Hartree-Fock and OEP ionization energies in an exchange-only calculation should be nearly identical.

Thus the OEP method not only provides the possibility of overcoming most of the important shortcomings of DFT that employ E_{xc} that are explicit functionals of only the spin densities as well as makes significant connections to the HF method in the limit of exchange-only calculations.

However, despite the fact that this alternative method of performing KS calculations of the effective local potential had been available as early as a decade before the HK and KS articles at least for the exchange-only case⁽²⁰⁾ and rederived two decades later,⁽²¹⁾ it was not generally employed because of the difficulty of solving the integral equation for the OEP.

II. The Krieger-Li-Iafrate (KLI) Approximation to the Optimized Effective Potential

We have shown⁽¹⁴⁾ that for an arbitrary $E_{xc}[\{\phi_{i\sigma}\}]$, an approximate solution to the OEP integral equation may be written for real occupied orbitals $\{\phi_{i\sigma}\}$ for a system with arbitrary symmetry

$$V_{xc\sigma}^{KLI}(\mathbf{r}) = \sum_i \frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})} [v_{i\sigma}(\mathbf{r}) + (\bar{V}_{xc\sigma i} - \bar{v}_{i\sigma})] \quad (5)$$

Here

$$v_{i\sigma} \equiv \frac{\delta E_{xc}[\{\phi_{i\sigma}\}]}{f_{i\sigma} \phi_{i\sigma}^* \delta \phi_{i\sigma}} \quad (6)$$

where $f_{i\sigma}$ is the fractional occupancy of the $i\sigma$ state and $v_{i\sigma} \equiv 0$ if $f_{i\sigma} \equiv 0$. Equation (5) was obtained by generalizing the results of an earlier ⁽²²⁾ exchange-only theory and results from making an exact transformation of the OEP integral equation and then setting some terms, whose average value are separately zero, to zero. Other less rigorous derivations have also been provided by KLI.^(23,24)

Equation (5) is still an integral equation because the expectation value of the unknown $V_{xc\sigma}$ appears on the right-hand-side. However, the exact solution of this equation may be written down explicitly⁽¹⁴⁾ in terms of the $\{n_{i\sigma}\}$ and $\{v_{i\sigma}\}$. Alternatively, one can solve for the unknown constants in eq. (5) by multiplying both sides by $n_{j\sigma}$ and integrating over r each occupied orbital. The resulting set of linear equations may then be solved using programs for sets of linear equations.

We⁽¹⁴⁾ have carefully investigated the analytic properties of the KLI approximation to the OEP. We find that for any $f_{m\sigma} > 0$

$$\bar{V}_{xc\sigma}^{KLI} = \bar{v}_{m\sigma} \quad (7)$$

where the average values are calculated using the KLI $\{\phi_{i\sigma}\}$ which are the solutions of the KS single particle equations with the exchange correlation potential given by $\bar{V}_{xc\sigma}^{KLI}$. Thus $\bar{V}_{xc\sigma}^{KLI}$ satisfies the analogous equations to eq. (1). It then follows as in the exact OEP calculations that $\epsilon_{m\sigma} = \bar{\epsilon}_{m\sigma}^{MP}$, and in the limit of slowly varying density $V_{xc\sigma}^{KLI} \rightarrow \frac{2}{3}V_{xc\sigma}^S$ and that, if $E_{xc}[\{\phi_{i\sigma}\}]$ includes the SIC terms that cancel the self-Hartree terms, $V_{xc\sigma} \rightarrow -1/r$ as $r \rightarrow \infty$. Furthermore, in the exact exchange-only case, Koopmans' theorem is still satisfied and in the general case there is an integer discontinuity in $V_{xc\sigma}^{KLI}$ as a new spin subshell begins to be occupied. Thus all the exact analytic properties satisfied by the exact OEP are maintained by the KLI approximation with the exception of Janak's theorem which is now approximately satisfied.

In addition we have performed a series of numerical calculations to test the accuracy of the KLI approximation in comparison with numerical calculations using the exact OEP in the one case in which previous work with the exact OEP had been performed i.e. spherically symmetric atoms in the exchange only approximation.^(21,25)

We^(13, 14, 26) have demonstrated that for such systems from He($Z = 2$) to Ba($Z = 56$), Au($Z = 79$) and Hg($Z = 80$) the KLI results for the total energy of the system is only 1/4 to 1/3 higher than the OEP results compared to the OEP overestimate of the spin unrestricted Hartree-Fock (SUHF) energy which varies from 50ppm for the lightest atoms to 2 ppm. In addition for $Z \leq 20$ the KLI eigenvalues for the HOMO, ϵ_m , are on average within 0.2% of the exact OEP results which are within 0.1% of the SUHF results and the KLI ionization energies, I , are within .05 mH of the OEP calculations which are about 0.25 mH from the SUHF results. Furthermore, expectation values of $\langle r^2 \rangle$ and $\langle r^{-1} \rangle$ and the electron density at the nucleus are different from the OEP results by 0.15%, 0.02% and 0.02% respectively. For atoms with $Z > 20$ similar results obtain except that for atoms in the first and second transition series in which there is nearly an s – d degeneracy the KLI approximation yields results for ϵ_m and $\langle r^2 \rangle$ which are typically $\approx 1\%$ from the OEP results. In addition the discrepancy in the values of I in the KLI approximation are then of O (0.5 mH). The only significant error in the KLI results is in the calculation of $m(0)$, the spin density at the nucleus, for atoms that have no unpaired s electrons but are spin polarized such as N and P. In such cases the spin density at the nucleus arises because electrons in spin polarized subshells (in this case p electrons) slightly polarize the s electrons which make a very small contribution to the separate spin densities. Thus, for example, although the KLI approximation yields separate spin densities at the nucleus of N which are accurate to 0.2%, the value of $m(0)$, which depends on the difference of these two numbers, doesn't even have the correct sign.⁽²⁶⁾

Even more remarkable than the atomic results are the results for singly charged negative ions which aren't even stable when the LSD approximation or its gradient corrected versions are employed. We find^(14, 27) that in the KLI approximation for $Z \leq 20$, on average ϵ_m is accurate to 0.2 mH while the electron affinity is within 0.05 mH of the exact OEP results. In addition the expectation values of $\langle r^2 \rangle$, $\langle r^{-1} \rangle$ and the density at the origin are within 0.5%, 0.02% and 0.2%,

respectively. Furthermore, when the KLI approximation is employed in calculations of heavier singly charged negative ions these results are essentially unchanged. The agreement between the OEP and KLI results for total energies and single particle properties for positive ions is even better than that for neutral atoms and negative ions because the effects of electron-electron interaction are reduced compared to the electron-nuclear attraction.⁽¹⁴⁾

In addition, we have shown by direct numerical calculation that the discontinuity in the OEP and KLI potentials are nearly identical when a new spin subshell begins to be filled.⁽¹⁴⁾ Moreover, by studying how the potential changes we have been able to show that the bumps in the exact OEP are remnants of the integer discontinuity in $V_{xc\sigma}^o$.^(14, 28)

In order to test the accuracy of the KLI approximation for functionals other than in the exact exchange only case, we have performed detailed comparisons between the results of an exact numerical OEP calculation and the KLI results for the case of an energy functional given by the local-spin-density approximation with Perdew-Zunger⁽⁴⁾ self-interaction-correction (LSDSIC) for the exchange-correlation energy. We⁽²⁹⁾ have demonstrated that the KLI approximation is equally valid in this case as well. We find that both the OEP and KLI are remarkably similar for atoms with $Z = 1$ to 20. In addition we find excellent agreement between the calculated total energies as well as quantities that are strongly related to the behavior of the valence electrons and are nearly identical in both OEP and KLI calculations, i.e. the difference between the $\langle r^2 \rangle$ and ϵ_m is less than 0.2% on average while the difference between the calculated I is less than 0.2 mH on average with the corresponding difference if only 0.1 mH for A.

The KLI method has also been applied to the self-consistent calculation of ionization potentials and electron affinities for atoms for a wide variety of proposed exchange-correlation energy functionals. Our results⁽³⁰⁾ demonstrate that no single choice gives entirely reliable results for atoms with $Z = 1$ to 20 and that further research is required to develop more accurate functionals. In order to facilitate such research we⁽³¹⁾ have obtained the Kohn-Sham effective potentials for the spin polarized lithium isoelectronic electronic series ($Z = 3-10$) and for the nitrogen atom. Configuration interaction (CI) and spin-unrestricted Hartree-Fock (SUHF) densities were used as input and the Kohn-Sham effective potentials for spin-majority and –

minority channels were deduced, from which the exchange and correlation contributions were obtained. In addition, accurate values were obtained for quantities such as exchange and exchange-correlations energies, Kohn-Sham orbital energies and kinetic contributions to exchange and correlation energies. These benchmark results can be used to provide rigorous tests on any future proposed exchange-correlation energy functional.

We⁽³²⁾ have also employed the KLI method to make an ab-initio theoretical determination of the exact-exchange mixing parameter in Becke's⁽³³⁾ exchange-correlation energy functional. This was accomplished by requiring that the parameter be chosen such that condition (4) of the foreword be satisfied as closely as possible for atoms with $Z \leq 20$, i.e. that the calculated ϵ_m equal the negative of the calculated ionization energy. We found that the calculated parameter was very close to the results obtained by Becke's empirical fit and also provided excellent results when applied to the electron affinity of the same atoms.

We⁽³⁴⁾ have also shown that it is possible to achieve essentially the same level of accuracy as that provided by an exact OEP or KLI calculation for properties primarily determined by the valence electron distribution by making a simple approximation. We have found that if the exchange energy functional is written as $E_X^{HF} = E_{CC}^{HF} + E_{CV}^{HF} + E_{VV}^{HF}$ where v corresponds to "valence" electrons which are taken to be those occupied orbitals in the last two subshells of an atom and c corresponds to all the other "core" electrons, then one may approximate E_{CC}^{HF} by E_X^{LSD} or E_X^{LSDSIC} . When such an approximation is made the required number of HF overlap integrals is significantly decreased while the values of I , A , ϵ_m and $\langle r^2 \rangle$ remain essentially unchanged.⁽³⁴⁾ This method should prove useful in future calculations of the bond strengths in complex molecules.

Most significantly, we have extended the application of the KLI method to the calculation of the properties of molecules^(35, 36) employing both the exact-exchange only functional as well as the LSDSIC exchange functional as was done in the atomic case. We have found that the KLI-HF results for the total energy for both homopolar and heteropolar diatomic molecules were as close to the exact HF results as they were for atoms. In addition, we have demonstrated that

the ϵ_m were also as accurately given by the KLI approximation thus making this method the only systematic, parameter free, approach to the calculation of molecular properties when orbital dependent exchange-correlation energy functionals are employed.

Since these results were presented, this method has been employed by many other investigators, the most interesting that provided by Engel et.al.⁽³⁷⁾ These authors performed HF-KLI calculations and compared them with the results of so-called "exact" OEP-HF reported by Ivanov et.al.⁽³⁸⁾ who attempted to solve the OEP integral equation using a basis set expansion for both the potential and the wavefunctions. Engel et. al. found that in every case the KLI results for the total energy were lower than the "exact" results, thus demonstrating that the latter were not as good an approximation since by definition the exact OEP results for the energy are the lowest possible when the wavefunctions are calculated as eigenfunctions of a single local multiplicative potential. Moreover, Engel et. al. also found that the dissociation energy for 10 diatomic molecules calculated using the KLI approximation were very close ($< .02$ ev) to the HF results, whereas the results of another "exact" calculation⁽³⁹⁾ were significantly different. In addition our⁽⁴⁰⁾ earlier investigation of the band structure of noble gas and alkali solids have demonstrated that the KLI approximation yields almost identical results as an exact HF calculation and provides the proper discontinuity that yields accurate band gaps

Thus, we have shown that the KLI approximation is robust, providing a highly accurate method for the calculation of atomic, molecular and solid state properties.

III Construction and Application of an Accurate Self-Interaction-Corrected Correlation Energy Functional Based on an Electron Gas with a Gap.

Since the KLI approximation yields results for the exchange-only KS theory that are at least an order of magnitude more accurate than that required by quantum chemistry accuracy criterion (1 kcal/mol for the dissociation energy), we have turned our attention to the development of an accurate correlation energy functional that would be appropriate for systems for which there is an energy gap between the highest energy occupied state and the lowest energy unoccupied state, e.g. atoms, molecules and semiconductors as opposed to metals on which

conventional density functional approximations are based. When the LSD approximation is applied to atoms, the calculated correlation energy is too large in magnitude by approximately a factor of two. As early as 1970, Dr. Walter Kohn, the father of density functional theory (Nobelist, 1999) pointed out that the large discrepancy between atomic correlation energies using the local density approximation (LDA) and the accurate (but difficult to perform) correlation energy calculated using quantum chemistry techniques was probably due to the lack of an energy gap in the derivation of the LDA⁽⁴¹⁾ correlation energy functional.

In collaboration with Dr. Andreas Savin (CNRS, Paris) we⁽⁴²⁾ have for the first time been able to construct a correlation energy functional based on an electron gas with an energy gap. In applying this to any quantum system we have made use of the fundamental theorem of Hohenberg and Kohn⁽¹⁾ that the correlation energy functional can be written as a functional of the electron density. Thus, we have chosen the gap to be $(1/8) |\nabla \ln n|^2$ which is non-negative and reduces to the ionization energy in the large r limit as well as approximately reduces to the excitation energy of the core electrons for r near the atomic nuclei. We have developed a spin density functional theory by interpolating between the unpolarized and completely polarized cases by employing the von Barth-Hedin formula.⁽⁴³⁾ We have found that the resulting functional reduces the LSD error by more than a factor of two. In addition, we have added a self-interaction-correction⁽⁴⁴⁾ (SIC) which is invariant to a unitary transformation of the occupied orbitals. This correction, entirely missing from the usual homogenous electron gas theory, is important in systems in which there are regions with only a few localized electrons as in the case for valence electrons in atoms and molecules. We find that the SIC functional yields correlation energies for atoms and molecules that are $\approx 15\%$ larger in magnitude than the exact results. Furthermore, we have added a gradient correction whose form is based on the requirement satisfied by the unknown exact functional that the functional should saturate under uniform scaling of the density and have the correct gradient expansion to lowest order in the high density limit. The resulting functional is then found to yield correlation energies that are correct to within a few percent for atoms and singly charged positive ions which is a greater accuracy than any other first principles correlation energy functional. Finally, in collaboration with Dr. Stefan Kurth, we⁽⁴⁵⁾ have improved on our functional by imposing the condition that the small gradient expansion satisfy the known exact result not merely in the large density limit but for densities as

small as those found in atoms and molecules. The improved functional not only yields improved correlation energies for atoms and positive ions, but also yields atomization energies for 20 small molecules that are on average in error by ≈ 3.4 kcal/mole compared to an average error of ≈ 32 kcal/mole when the LSD approximation is employed. Moreover, the results for the surface energy of jellium over a wide range of densities is accurate to within only a few percent when compared to exact results whereas nearly all other correlation energy functionals yield results that are significantly in error for this quantity.

In addition, we have come to realize that highly accurate results employing density functional theory can be obtained only through the explicit inclusion of contributions to the correlation energy from low lying virtual states above the occupied orbitals. These contributions have in general been ignored in density functionals for the correlation energy and would be difficult to insert in a theory based on a uniform electron gas without a gap. However, our functional enables such contributions to be included. In collaboration with Dr. Savin and Ms. Claudine Gutle, we^(46,47) have found by employing second order perturbation theory that for atoms for which there are no virtual states corresponding to a two electron excitation that is nearly degenerate with the ground state, e.g. helium and lithium, that the inclusion of the virtual localized states (using KLI perturbation theory) gives a negligible contribution to the correlation energy. However, for atoms for which there are doubly excited virtual states which are nearly degenerate with the ground state, e.g. beryllium, boron and carbon, there are significant contributions to the correlation energy from these localized virtual states. In fact the contributions are so large that they can be accurately calculated only by treating them as quasi-degenerate and using nearly degenerate perturbation theory. These considerations have recently been extended⁽⁴⁸⁾ to a study of the isoelectronic series for neon, magnesium and argon. Since the addition or subtraction of only one electron ion significantly change the existence of these states, they must be taken into careful consideration when calculations of chemical bonding are made.

We are currently trying to develop a consistent method of incorporating these results into our functional obtained from an electron gas with a gap. In addition, we⁽⁴⁹⁾ have recently completed constructing a new correlation energy functional based on an electron gas with a gap but with a density of states in the continuum that varies as the square root of the energy above

the gap as is the case for atoms, molecules and semiconductors. The combination of these functionals along with the inclusion of contributions from the virtual localized states is being carefully studied and is expected to lead to improved results for atomic and ionic correlation energies as well as for atomization of molecules.

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List of Inventions

None

Publications

- 1) Recent Developments in Kohn-Sham Theory for Orbital Dependent Exchange-Correlation Energy Functionals, J.B. Krieger, Y. Li and G.J. Iafrate (in "Density Functional Theory" eds. R.M. Dreizler and E.K.U. Gross, Plenum Press, New York, 1995) p. 191
- 2) Kohn-Sham Theory for Orbital Dependent Exchange-Correlation Energy Functionals: Application to the Calculation of Ionization Potentials and Electron Affinities, J.B. Krieger, J. Chen, Y. Li and G.J. Iafrate, *Int. J. Quant. Chem. Quantum Chemistry Symposium* **29**, 79 (1995).
- 3) Kohn-Sham Potentials for Spin Polarized Systems, J. Chen, J.B. Krieger, R.O. Esquivel, M.J. Stott and G.J. Iafrate, *Phys. Rev. A* **54**, 1910(1996)
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- 6) Theoretical Determination of the Exact-Exchange Mixing Parameter, J.B. Krieger, J. Chen and G.J. Iafrate, *Int. J. Quant. Chem.* **69**, 255 (1998).
- 7) Construction of an Accurate Self-Interaction-Correlation Energy Functional Based on an Electron Gas with a Gap, J.B. Krieger, J. Chen, G.J. Iafrate and A. Savin, "Electron Correlations and Materials Properties", eds. A. Gonis, H. Kioussis, and M. Ciftan, p463, Kluwer Academix/Plenum Publications (1999).
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- 9) Construction and Application of an Accurate Self-Interaction-Corrected Correlation Energy Functional Based on an Electron Gas with a Gap. J.B. Krieger, J. Chen and S. Kurth. "Density Functional Theory and its Applications to Materials", eds. V. Van Doren, C. Van Alsenoy and P. Geerlings p.48, American Institute of Physics (AIP Conference Proceedings 577) (2001).
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- 11) Coupled-Cluster Calculations using Local Potentials, C. Gutle, J.L. Heully, J.B. Krieger and A. Savin, Phys. Rev. A (accepted for publication).
- 12) Improved Correlation Energy Functional from an Electron Gas with a Gap. C. Gutle, A. Savin and J.B. Krieger (in preparation)

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